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Benzene and Aromatic Compounds

CHAPTER 16

MASTERING ORGANIC CHEMISTRY

- Understanding the MO Energy Levels for Planar, Cyclic, Conjugated Compounds
- Using Hückel's Rule to Predict Whether a Compound Is Aromatic, Antiaromatic, or Neither
- Understanding How Aromaticity and Antiaromaticity Affect the Chemical Behavior of Compounds

BENZENE OCCUPIES a special place in the field of organic chemistry. It is an especially stable compound, and because of this stability, substituted benzenes are widely distributed among natural products and industrial chemicals. Efforts by organic chemists to understand this stability have contributed significantly to our current models for the electronic structure of organic compounds and have led to the development of theories that not only explain the special properties of benzene but also help to explain and predict which other compounds have this special stability that has come to be called aromaticity.

This chapter begins with a discussion of some experimental observations that support the conclusion that benzene is especially stable. Then a model based on molecular orbital theory is presented to explain this stability. This model is generalized so that it can be applied to other compounds that are especially stable and also to some that are especially unstable. Several different classes of such compounds are discussed, along with examples of a variety of experimental observations that can be rationalized based on this theory.

16.1 BENZENE

Benzene was discovered in 1825 by Michael Faraday, who isolated it from the liquid that condensed from the gas that was burned in the street lamps of London. Although Faraday was able to deduce that the formula of benzene is C_6H_6, it was not until 1866 that the correct structure was proposed by Kekulé (see the Focus On box in Chapter 12 on page 469).

From the beginning, it has been apparent that benzene does not behave like an alkene. For example, the addition

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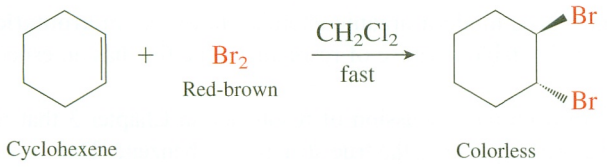
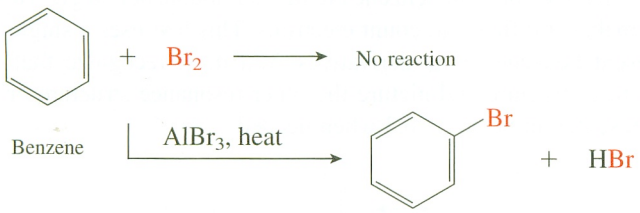
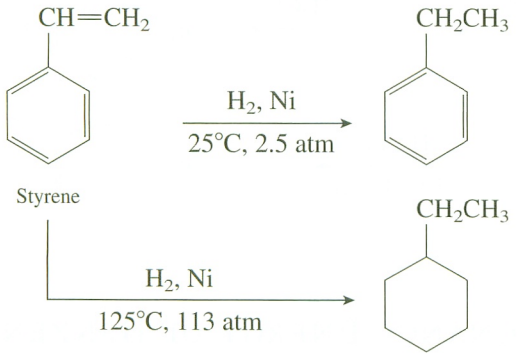
of bromine to alkenes and the use of this reaction as a test for the presence of a carbon–carbon double bond was described in Section 11.4. Thus, when bromine is added to a solution of an alkene, such as cyclohexene, in dichloromethane, a rapid reaction causes the red-brown color of the bromine to quickly disappear. The product results from addition of the bromine to the double bond.



In sharp contrast, benzene is unreactive with bromine under these same conditions. Under more vigorous reaction conditions (the presence of a Lewis acid catalyst, such as aluminum tribromide, and higher temperature), benzene does react with bromine. However, the product results from a substitution of a Br for a H, rather than addition of Br_2 to one of the double bonds. The product retains the benzene structure of three conjugated double bonds in a six-membered ring:



Another example is provided by the catalytic hydrogenation reaction described in Section 11.12. When a compound such as styrene is reacted with hydrogen and a catalyst at room temperature and relatively low pressure, only the alkene double bond reacts. The aromatic ring is inert under these conditions. Styrene reacts with hydrogen to form a cyclohexane ring only under much more vigorous conditions employing higher temperature and pressure:



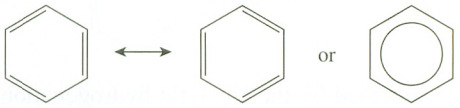
The slowness of the reaction of benzene with bromine and the vigorous conditions required for its catalytic hydrogenation show that it is much less reactive than an alkene. In fact, until recent concerns about its carcinogenicity developed, benzene was used as a solvent for many organic reactions because of its low reactivity. When reaction with

bromine is forced to occur, the formation of a substitution product, rather than an addition product, illustrates the stability of the six-membered aromatic ring. Such substitution reactions are typical of aromatic compounds and are discussed extensively in Chapter 17.

As mentioned in Section 12.1, the term *aromatic* was originally applied to substituted benzene derivatives because they have more pleasant odors than do many other organic compounds. To a modern organic chemist, however, an **aromatic compound** is one that is especially stable because of resonance, one that has an especially large resonance energy.

You are aware from the discussion of resonance in Chapter 3 that no single Lewis structure satisfactorily represents the true structure of benzene. There is no alternation in bond length as one proceeds around the ring, as would be implied by a single structure. All of the carbon–carbon bonds of benzene are the same length (1.4 Å), intermediate between the length of a single bond (1.5 Å) and the length of a double bond (1.3 Å).

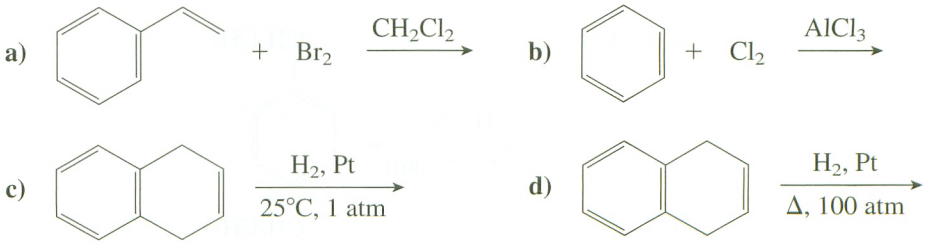
Benzene has two major resonance structures that contribute equally to the resonance hybrid. These are sometimes called **Kekulé structures** because they were originally postulated by Kekulé in 1866. You may also encounter benzene written with a circle inside the six-membered ring rather than the three double bonds. This representation is meant to show that the bonds in benzene are neither double nor single. However, the circle structure makes it difficult to count electrons. This text uses a single Kekulé structure to represent benzene or its derivatives. You must recognize that this does not represent the true structure and picture the other resonance structure or call upon the MO model presented in Section 16.3 when needed.



Kekulé structures

PROBLEM 16.1

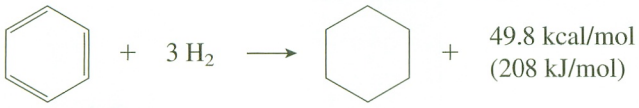
Show the products of these reactions:



16.2 Resonance Energy of Benzene

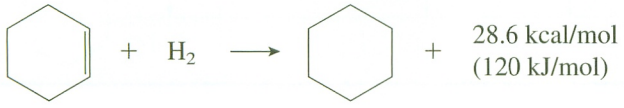
The bromination and hydrogenation reactions just discussed, along with much other evidence, indicate that benzene has an especially large resonance stabilization. Can the magnitude of this resonance stabilization be determined? One way to measure such a stabilizing effect in a compound is to measure the amount of heat evolved in some re-

action that destroys the effect and compare it to that evolved in the same reaction of some model compound where the stabilizing effect is absent. In the case of benzene the resonance stabilization is lost when it is saturated by catalytic hydrogenation. Reaction of one mole of benzene with three moles of hydrogen is an exothermic reaction and produces cyclohexane and 49.8 kcal/mol (208 kJ/mol) of heat.



Benzene

What compound should be used in the hydrogenation as the model for the hypothetical compound "cyclohexatriene"—that is, benzene without any resonance stabilization? The model should be as similar to benzene as possible but without any possible resonance stabilization. The best that can be done is to use the double bond of cyclohexene as the model for one double bond of benzene. Hydrogenation of cyclohexene produces cyclohexane and 28.6 kcal/mol (120 kJ/mol) of heat:



Cyclohexene

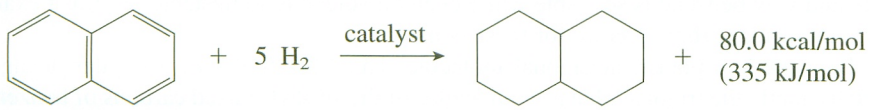
According to this model, the hydrogenation of the three "double bonds" of benzene should produce $3 \times 28.6 = 85.8$ kcal/mol (359 kJ/mol) of heat if there were no resonance stabilization. The difference between the amount calculated on the basis of three cyclohexene double bonds and the amount that is actually produced is the resonance stabilization for benzene. By using these reactions, the resonance energy or resonance stabilization of benzene is calculated to be 36.0 kcal/mol (151 kJ/mol):

Heat evolved from the reaction of 3 C=C without resonance stabilization (3 × 28.6 kcal/mol)	85.8 kcal/mol (359 kJ/mol)
Minus heat evolved from the reaction of 3 C=C of benzene	−49.8 kcal/mol (208 kJ/mol)
Equals the resonance stabilization of benzene	36.0 kcal/mol (151 kJ/mol)

This is a significantly larger resonance stabilization than is found in other types of compounds that are not termed aromatic. Figure 16.1 shows a diagram of the energies of these hydrogenation reactions.

PROBLEM 16.2

The catalytic hydrogenation of naphthalene produces 80.0 kcal/mol (335 kJ/mol) of heat. Calculate the resonance stabilization of naphthalene. Do you think naphthalene should be termed aromatic?



Napthalene

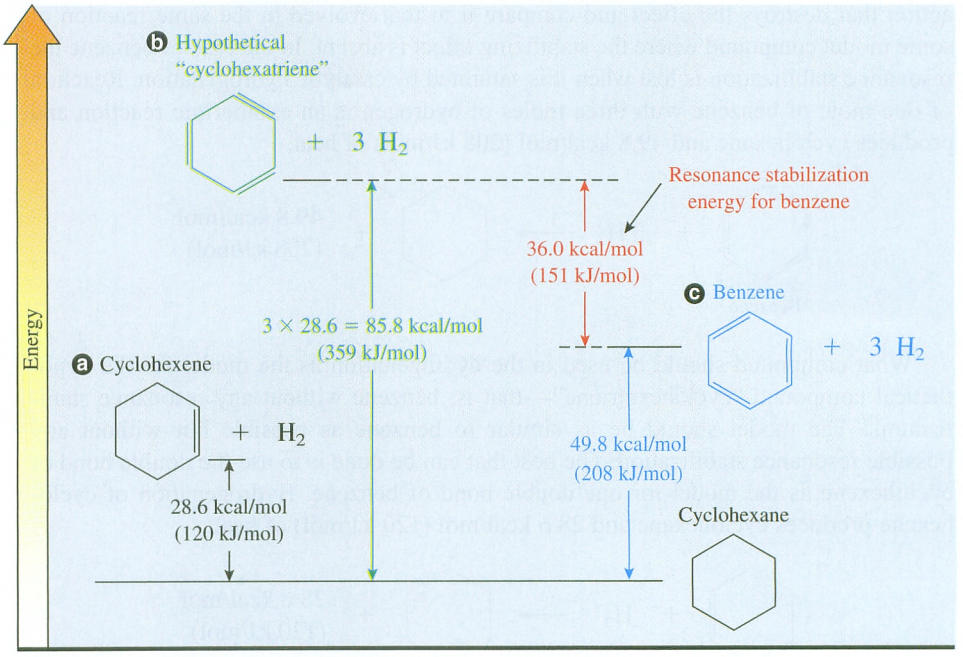


Figure 16.1

DIAGRAM OF THE ENERGIES OF HYDROGENATION OF ⓐ CYCLOHEXENE, ⓑ HYPOTHETICAL "CYCLOHEXATRIENE," AND ⓒ BENZENE.

16.3 MOLECULAR ORBITAL MODEL FOR CYCLIC CONJUGATED MOLECULES

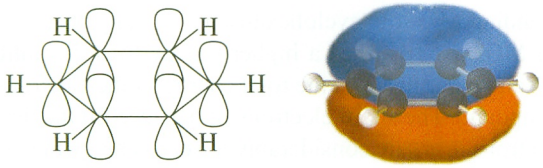
Although resonance is one of the most useful concepts in organic chemistry, one of the areas in which it is inadequate is in the explanation of aromaticity. For example, resonance structures similar to those of benzene can be written for cyclobutadiene:

Cyclobutadiene

On the basis of this resonance picture only, organic chemists initially expected that cyclobutadiene, like benzene, would have a large resonance stabilization and would be especially stable. Yet cyclobutadiene proved to be an extraordinarily elusive compound. Many unsuccessful attempts were made to prepare this compound before it was finally synthesized at very low temperature in 1965. The compound is quite unstable and reacts rapidly at temperatures above 35 K. As we shall see, cyclobutadiene is a member of an unusual group of compounds that are actually destabilized by resonance. To understand why benzene is so stable while cyclobutadiene is so unstable, we must examine a molecular orbital picture for these compounds.

Benzene is a planar, hexagonal molecule. The 120° angles of a regular hexagon match exactly the trigonal planar bond angles of the sp^2-hybridized carbons of benzene, so it has no angle strain. There is a p orbital on each carbon that is perpendicular to the

plane of the ring carbons. This results in an overlapping cycle of conjugated p orbitals that extends completely around the ring.



Recall from Section 3.6 that molecules such as benzene that have a series of conjugated p orbitals cannot be described very well by localized molecular orbitals that extend over only two atoms at a time. Instead, delocalized pi MOs that extend over the entire group of conjugated p orbitals must be employed. For benzene, all six of the p atomic orbitals combine to form six delocalized MOs. The number of MOs equals the number of AOs that overlap to form them.

Let's compare the molecular orbital picture for benzene to that for the imaginary "cyclohexatriene" in which the double bonds are not conjugated. As shown in Figure 16.2, each of the three "nonconjugated" double bonds of "cyclohexatriene" would have a pi bonding MO and a pi antibonding MO at the same energies as the pi MOs of ethene. This results in a total of six MOs: three degenerate bonding MOs and three degenerate antibonding MOs. (Recall that MOs that have the same energy are said to be degenerate.) The energies of the bonding and antibonding MOs are symmetrically placed about the energy of a nonbonding p orbital, which is, by convention, assigned a value of zero.

Calculations using a simple version of molecular orbital theory show that the energies of the six delocalized pi MOs of benzene are arranged somewhat differently. The lowest-energy MO, designated π_1, is significantly lower in energy than the bonding

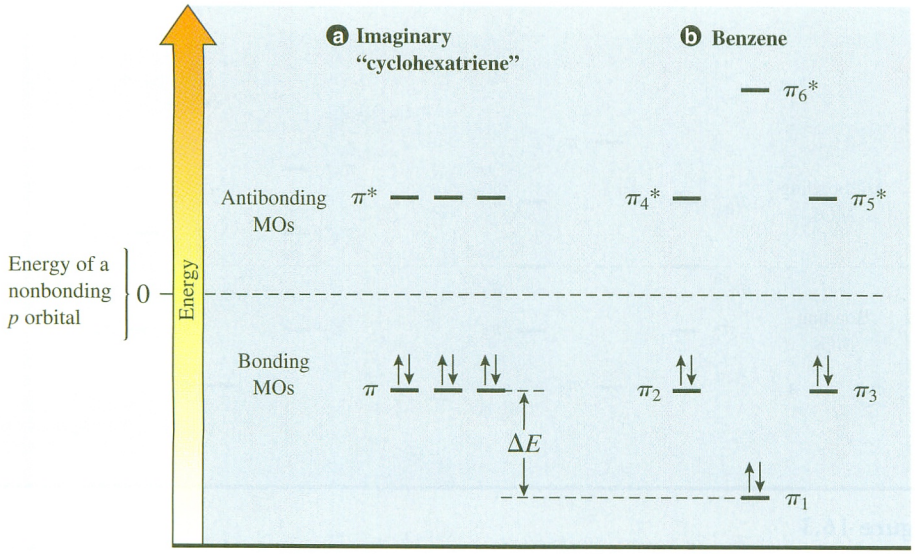
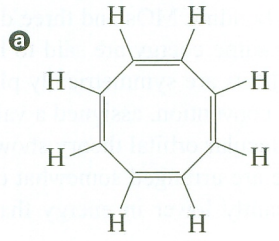


Figure 16.2

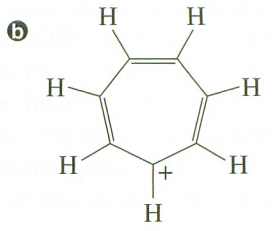
ENERGIES OF THE PI MOLECULAR ORBITALS OF (a) IMAGINARY "CYCLOHEXATRIENE" COMPARED TO THOSE OF (b) BENZENE.

MOs of "cyclohexatriene" (see Figure 16.2). Then there are two degenerate bonding MOs, designated π_2 and π_3, that have the same energy as the bonding MOs of "cyclohexatriene." Next are two degenerate antibonding MOs, π_4* and π_5*, that have the same energy as the antibonding MOs of "cyclohexatriene." Finally, there is a single highest-energy antibonding MO, π_6*, that has a higher energy than the antibonding MOs of "cyclohexatriene." Remember that it is the total energy of the electrons that determines the stability of a compound. The six pi electrons of benzene fill the three bonding MOs. Because the two electrons in π_1 are considerably lower in energy than their counterparts in "cyclohexatriene," benzene is more stable by $2\Delta E$. This extra stabilization is what we have previously termed the resonance energy of benzene.

Calculations for other cyclic conjugated molecules show that the energies of their pi molecular orbitals are arranged in patterns similar to that of benzene. All such compounds have one lowest-energy MO, followed by pairs of degenerate MOs at increasingly higher energies. If the total number of MOs is even, then there is one highest-energy MO and the MOs are arranged symmetrically about zero energy, as is the case with benzene. This arrangement is illustrated for the eight MOs of cyclooctatetraene in Figure 16.3. (For the MOs of cyclooctatetraene to be symmetrically



Cyclooctatetraene



Cycloheptatrienyl carbocation

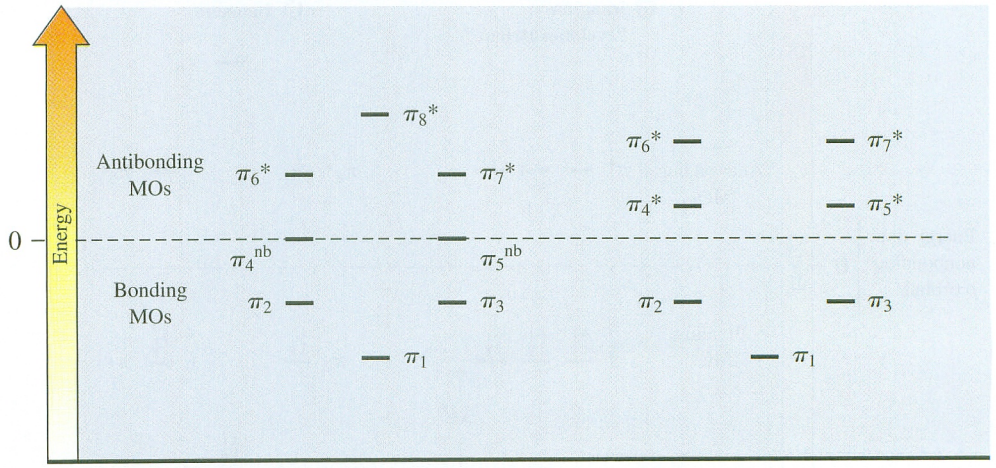


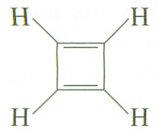
Figure 16.3

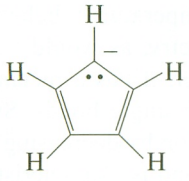
ENERGIES OF THE PI MOLECULAR ORBITALS OF (a) CYCLOOCTATETRAENE AND THE (b) CYCLOHEPTATRIENYL CARBOCATION. Note that the electrons are not yet shown in the MOs in these diagrams.

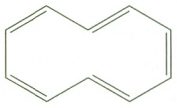
arranged about zero energy, it is necessary for one degenerate pair, π_4^{nb} and π_5^{nb}, to be located at zero energy. MOs at zero energy are termed nonbonding.) If the total number of MOs is odd, the pattern is the same with the exception that the highest-energy MO is absent. In this case the MOs can no longer be symmetrically arranged about zero energy. This arrangement is also illustrated in Figure 16.3 for the seven MOs of the cycloheptatrienyl carbocation. The exact energy of each MO is not as important as is the pattern of one lowest-energy MO and degenerate pairs with increasing energy.

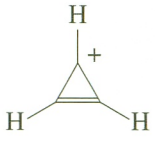
PROBLEM 16.3

Show the patterns for the pi MO energy levels for these compounds:

a) 

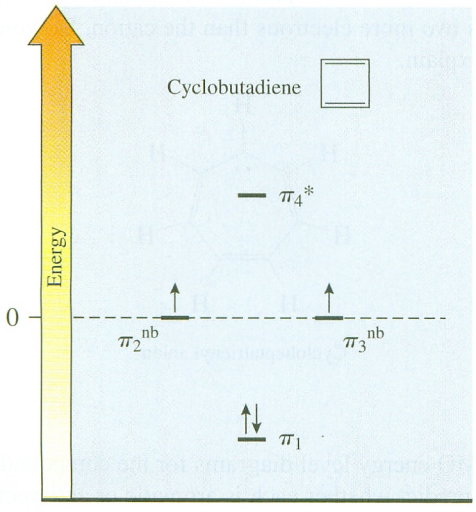
b) 

c) 

d) 

16.4 CYCLOBUTADIENE

Let's now examine the MO picture for cyclobutadiene and see whether we can discern why it is so much less stable than benzene. There are four *p* orbitals in cyclobutadiene, so there are four pi MOs. These must be arranged with one MO at lowest energy, two degenerate MOs at zero energy, and one MO at highest energy. There are four electrons in these MOs. Two of these electrons occupy the lowest-energy MO. According to Hund's rule, the two remaining electrons have the same spin and each occupies a different member of the degenerate pair of nonbonding MOs.



The difference between the electron arrangement in benzene and that in cyclobutadiene is the key to whether a cyclic, conjugated compound will be especially stable, like benzene, or especially unstable, like cyclobutadiene. Benzene has its ***h*ighest *o*ccupied *m*olecular *o*rbitals** (the highest-energy MOs that contain electrons, also known as **HOMOs**) completely filled with electrons. Cyclic compounds, completely conjugated around the ring, with filled HOMOs, such as benzene, are especially stable and are aromatic. In contrast, cyclobutadiene has only enough electrons that its HOMOs are half filled. Compounds with half-filled HOMOs such as cyclobutadiene are found to be especially unstable and are termed **antiaromatic.**

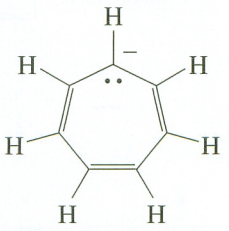
Cyclobutadiene is a highly reactive compound. As mentioned previously, numerous attempts to prepare it failed because of this high reactivity. However, it can be prepared and studied at very low temperatures, below 35 K. Such studies indicate that it does not have a square geometry, as would be suggested by the resonance structures shown on page 646. Rather, it has a rectangular geometry, with shorter double bonds alternating with longer single bonds. Such bond alternation relieves some of the antiaromatic destabilization by decreasing the overlap between the *p* orbitals where the longer bonds occur and is characteristic of compounds that are not aromatic. When a sample of cyclobutadiene is allowed to warm above 35 K, the molecules react rapidly to form dimers that are no longer conjugated and therefore are no longer antiaromatic.

PROBLEM 16.4

Add the appropriate number of electrons to the MO energy level diagram for cyclooctatetraene in Figure 16.3. Is this compound aromatic or antiaromatic?

PROBLEM 16.5

Add the appropriate number of electrons to the MO energy level diagram for the cycloheptatrienyl cation in Figure 16.3. Is this ion aromatic or antiaromatic? The cycloheptatrienyl anion has two more electrons than the cation. Do you expect this anion to be a stable species? Explain.



Cycloheptatrienyl anion

PROBLEM 16.6

Add electrons to the MO energy level diagrams for the compounds in parts b, c, and d of Problem 16.3, and predict whether each is aromatic or antiaromatic.

16.5 HÜCKEL'S RULE

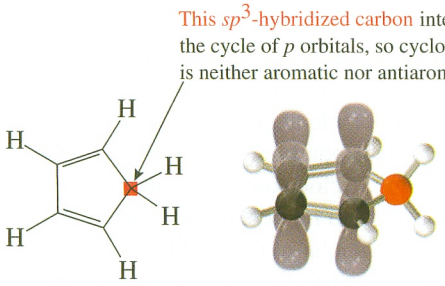
All cyclic, conjugated molecules have one lowest-energy pi MO and pairs of degenerate MOs at higher energies. Whether a compound is aromatic or antiaromatic depends on the number of electrons occupying these MOs. An aromatic compound has its HOMOs completely filled with electrons. Therefore, it must have two electrons in the lowest-energy MO plus some multiple of four electrons so that the HOMOs are filled. (Another way of stating this is that it must have an odd number of pairs of electrons, one pair for the lowest-energy MO and an even number of pairs to fill the occupied degenerate MOs.)

The criteria for a compound to be aromatic were developed by Erich Hückel.

HÜCKEL'S RULE

Cyclic, fully conjugated, planar molecules with $4n + 2$ pi electrons (n = any integer including zero) are aromatic.

Let's analyze each aspect of this rule. First, the molecule must have a ring with a series of conjugated p orbitals that extends completely around the cycle, like benzene. If the cycle of conjugated orbitals is interrupted, as in the case of cyclopentadiene, then the compound is neither aromatic nor antiaromatic. It is just an alkene.



Second, the ring must be planar so that the p orbitals overlap in pi fashion completely around the cycle. If the ring is not planar, the p orbitals are twisted so that they are not parallel, resulting in a decrease in overlap. This decreases or even eliminates the aromatic or antiaromatic effect of the conjugation.

Finally, the number of pi electrons must equal 2 plus a multiple of 4 (or $4n + 2$ pi electrons). Some of the possible numbers are as follows:

n	$4n + 2$	Number of pairs
0	2	1
1	6	3
2	10	5
3	14	7

As we have seen, benzene, with its six pi electrons (sometimes called an aromatic sextet), is the prototypical aromatic compound.

The criteria for an antiaromatic compound can be generalized in a similar manner. The requisite number of electrons to have the HOMOs half filled is a multiple of four (an even number of pairs). Therefore, cyclic, fully conjugated, planar molecules with $4n$ pi electrons are antiaromatic. Some of the possible numbers of electrons are as follows:

n	$4n$	Number of pairs
1	4	2
2	8	4
3	12	6

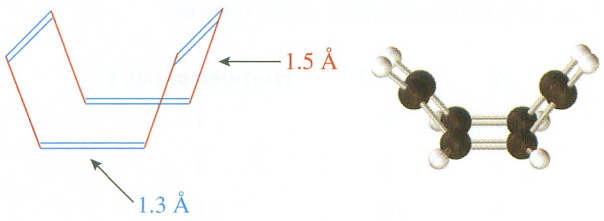
Some additional examples will help clarify this concept and illustrate its usefulness in predicting and explaining experimental observations.

PROBLEM 16.7

Use Hückel's rule to predict whether each of the compounds in problem 16.3 is aromatic or not.

16.6 CYCLOOCTATETRAENE

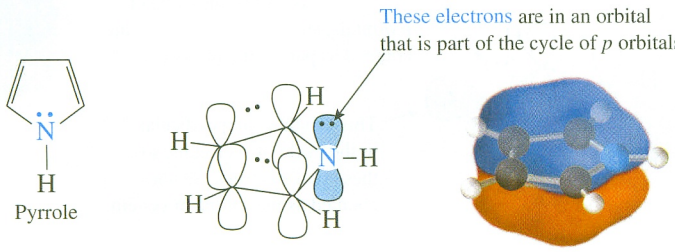
Cyclooctatetraene has four double bonds, so it has eight pi electrons. This is a multiple of 4, so cyclooctatetraene would be antiaromatic if it were planar. However, planar cyclooctatetraene would have considerable angle strain because its bond angles would be 135° rather than the trigonal planar bond angle of 120°. To relieve both antiaromatic destabilization and angle strain, cyclooctatetraene adopts a nonplanar, tub-shaped geometry. Each double bond is twisted relative to the adjacent double bonds so that the *p* orbitals of one are nearly perpendicular to those of the adjacent double bonds. Therefore, cyclooctatetraene behaves as a normal, nonconjugated alkene. It can be readily prepared and isolated, and it does not show any of the special instability associated with antiaromatic compounds. Nor does it have any features of the special stability associated with aromatic compounds. It exhibits bond alternation—that is, shorter double bonds alternating with longer single bonds—and reacts with bromine to give addition products. It is said to be nonaromatic.



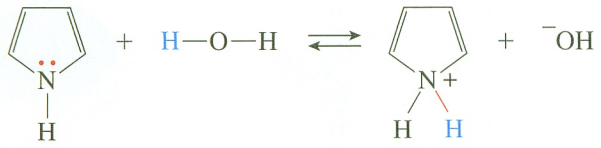
Cyclooctatetraene

16.7 Heterocyclic Aromatic Compounds

A heterocyclic compound is one that has an atom other than carbon as one of the ring atoms. The compound with a five-membered ring that has two double bonds and a nitrogen atom is called pyrrole.

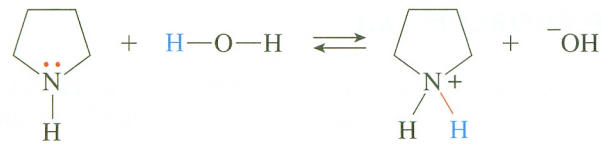


It is a planar molecule, and the pair of electrons on the nitrogen is in a *p* orbital that is parallel to the *p* orbitals of the ring double bonds. Therefore, pyrrole has a series of conjugated *p* orbitals that extend completely around the ring and that contain a total of six electrons: two from the nitrogen and four from the double bonds. It is an aromatic compound. On the basis of its heat of combustion, its aromatic resonance energy is calculated to be 21 kcal/mol (88 kJ/mol). It undergoes substitution reactions like benzene, rather than addition reactions like alkenes. Furthermore, it is much less basic than other amines. As can be seen in the following equation, the nitrogen of its conjugate acid does not have an electron pair to contribute to the cycle, so it is no longer aromatic. In other words, the electrons on the nitrogen of pyrrole are part of an aromatic sextet. If they are used to form a bond to a proton in an acid–base reaction, the aromatic stabilization of pyrrole is lost.



Aromatic Nonaromatic

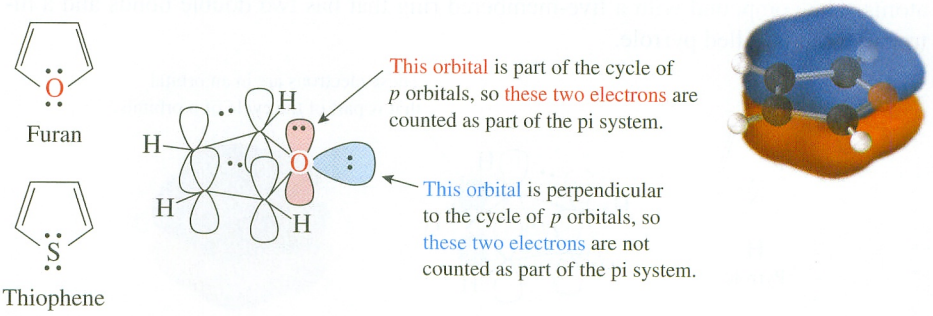
Pyrrole is about 10^{14} times weaker as a base than is pyrrolidine, the five-membered nitrogen heterocycle that has no double bonds, because the basic pair of electrons on the nitrogen of pyrrolidine is not part of an aromatic cycle.



Pyrrolidine

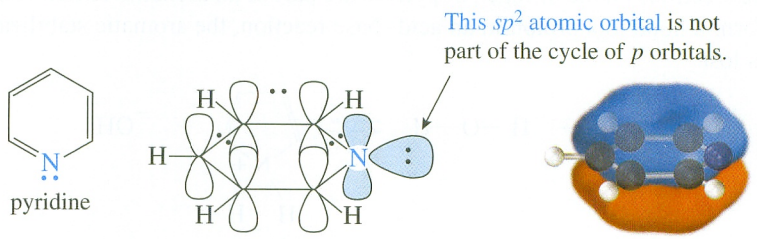
The oxygen analog of pyrrole is furan. In this case, one pair of electrons on the oxygen is part of an aromatic sextet while the other is in an sp^2 hybrid AO that lies in the plane of the ring and is not part of the aromatic cycle. The sulfur analog, thiophene, has a similar structure. Both furan and thiophene are aromatic compounds that exhibit sub-

stitution reactions. From their heats of combustion the resonance energies of furan and thiophene are calculated to be 16 kcal/mol (67 kJ/mol) and 29 kcal/mol (121 kJ/mol), respectively.


Furan
Thiophene
This orbital is part of the cycle of p orbitals, so these two electrons are counted as part of the pi system.
This orbital is perpendicular to the cycle of p orbitals, so these two electrons are not counted as part of the pi system.

The differing amounts of aromatic stabilization for benzene, pyrrole, furan, and thiophene demonstrate that aromatic stabilization occurs in varying degrees, depending on the structure of the compound. Some compounds have a large aromatic stabilization that dramatically affects their stabilities and chemical reactions. Others may have only a small stabilization and have stabilities and reactions that are more comparable to a normal alkene.

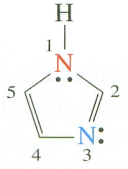
Pyridine has a six-membered ring containing a nitrogen atom and is the nitrogen analog of benzene. The electrons on the nitrogen are in an sp^2 orbital in the plane of the ring like the electrons of the carbon–hydrogen bonds and are not part of the cycle of pi electrons. Pyridine has six electrons in its pi MOs and is aromatic.



Because the unshared electron pair on the nitrogen is not part of the aromatic pi electron system, pyridine is a much stronger base than pyrrole. Recall that pyridine is used as a basic solvent in a number of reactions.

PRACTICE PROBLEM 16.1

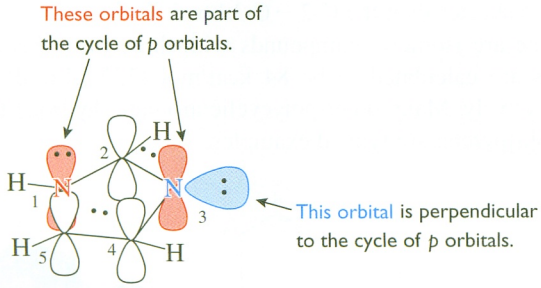
Determine which electrons of imidazole are in orbitals that are part of the conjugated cycle of *p* orbitals and which are not. Explain whether imidazole is aromatic or not.



Imidazole

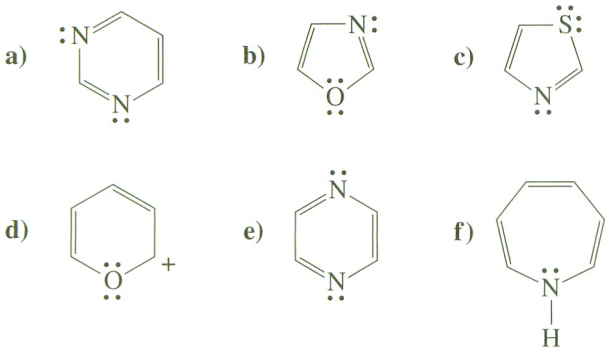
Solution

Nitrogen 1 (red) is like the nitrogen of pyrrole. Its electron pair is in a *p* orbital that is part of the conjugated cycle. In contrast, nitrogen 3 (blue) is like the nitrogen of pyridine. Its electron pair is in an sp^2 hybrid AO that is perpendicular to the conjugated cycle of *p* orbitals, so these electrons are not counted. (Only one orbital on an atom can be part of the conjugated cycle. Because the *p* orbital of the double bond is part of the cycle, the other orbital on N-3 cannot be part of the cycle.) Overall imidazole has six electrons in the cycle, the four electrons of the two double bonds, and the two electrons on N-1, so it is aromatic.



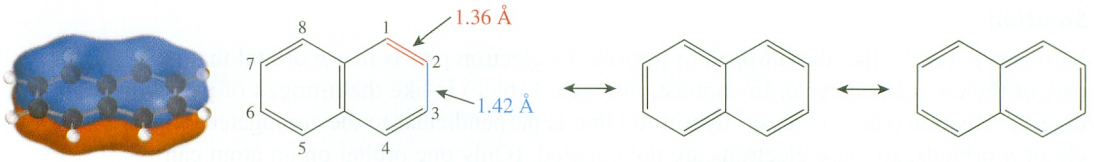
PROBLEM 16.8

Explain whether each of these compounds is aromatic, antiaromatic, or nonaromatic:



16.8 Polycyclic Aromatic Hydrocarbons

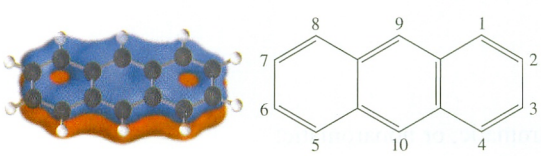
Polycyclic aromatic hydrocarbons have two or more benzene rings fused together. The simplest example is naphthalene. Hückel's rule does not apply to such fused ring systems. However, if the individual rings that are fused to form the polycyclic compound are aromatic, then the fused compound is also considered to be aromatic. Naphthalene, formed by fusing two benzene rings, is aromatic, although it is not expected to have as much resonance stabilization as two benzenes. This is confirmed experimentally. On the basis of its heat of combustion, the resonance energy for naphthalene has been calculated to be 61 kcal/mol (255 kJ/mol), a value that is larger than that of benzene (36 kcal/mol [151 kJ/mol]), although not twice as large.



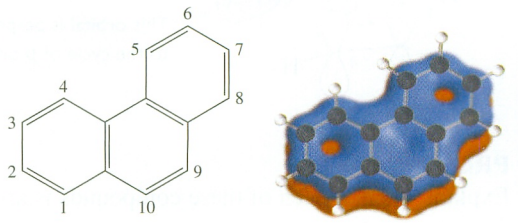
Naphthalene

Three resonance structures can be written for naphthalene. Note that the C-1—C-2 bond is a double bond in two of these structures and a single bond in one, while the C-2—C-3 bond is a single bond in two structures and a double bond in one. This explains why the C-1—C-2 bond is shorter than the C-2—C-3 bond.

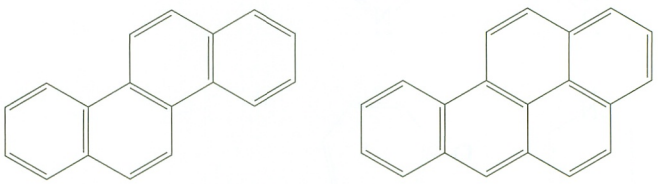
Anthracene and phenanthrene are isomeric compounds with three fused benzene rings. Their resonance energies are calculated to be 84 kcal/mol (352 kJ/mol) and 92 kcal/mol (385 kJ/mol), respectively. Many other polycyclic aromatic hydrocarbons are known. Chrysene and benzo[a]pyrene are typical examples.



Anthracene



Phenanthrene



Chrysene Benzo[a]pyrene

These compounds all possess considerable aromatic stabilization. They undergo substitution reactions like benzene, although some of them have pi bonds that are more reactive than those of benzene.

PROBLEM 16.9

Draw the five resonance structures for phenanthrene. Based on examination of these structures, which carbon–carbon bond of phenanthrene should be the shortest?

PROBLEM 16.10

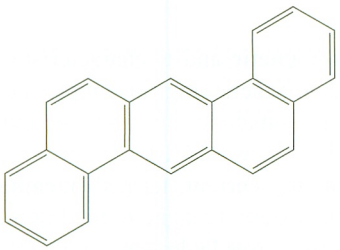
Reaction of phenanthrene with Br_2 produces $C_{14}H_{10}Br_2$. This reaction occurs at the bond with the most double bond character. Show the structure of this product. Qualitatively compare the amount of resonance energy lost on formation of this product to the amount that would be lost if the addition were to occur at a different bond.

Focus On

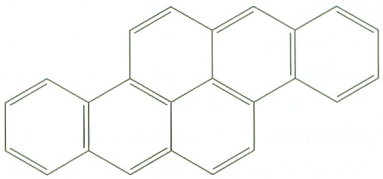
Carcinogenic Polycyclic Aromatic Hydrocarbons

The first case of an environmental carcinogen was identified by an English surgeon, Percivall Pott, in 1775. He recognized a high incidence of scrotal cancer among chimney sweeps and correctly identified the causative agent as the coal soot to which they were continuously exposed. In the 1930s, some of the polycyclic aromatic hydrocarbons (PAH) found in coal soot were proved to be carcinogenic.

Incomplete combustion of carbonaceous material produces a wide variety of polycyclic aromatic hydrocarbons because these compounds are relatively stable and have a high ratio of carbon to hydrogen. Some of the highly carcinogenic compounds that are produced are benzo[a]pyrene, dibenz[a,h]anthracene, and dibenz[a,h]pyrene. These compounds are produced by the combustion of fossil fuels and are also found in tobacco smoke and automobile exhaust.



Dibenz[a,h]anthracene

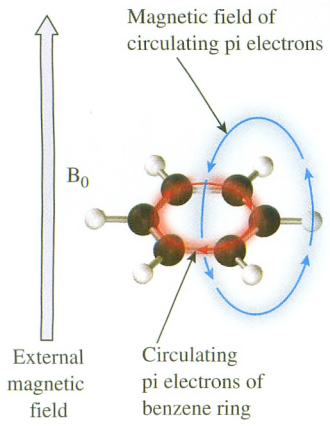


Dibenz[a,h]pyrene

Although the mode of action of these compounds is not completely known, one idea is that they bind to DNA by sliding between its aromatic bases. Then oxidation of a reactive double bond in the PAH produces an epoxide intermediate that reacts with the DNA to initiate the carcinogenic process.

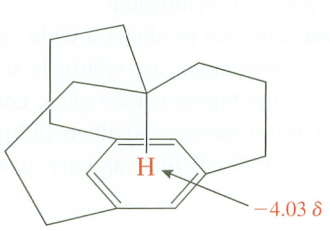
16.9 NMR AND AROMATICITY

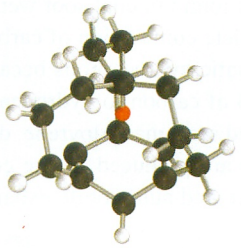
It can be difficult to determine whether some compounds have any aromatic character or not based on their chemical reactions, especially if the amount of aromatic stabilization is small. In such situations, NMR spectroscopy provides another useful criterion for aromaticity. As discussed in Chapter 14, the hydrogens on a benzene ring usually appear in the region of 7 to 8 δ in the ^{1}H-NMR spectrum, significantly downfield from the position for hydrogens on alkene double bonds. This downfield shift is a result of a "ring current" that results from circulation of the pi electrons when the molecule is placed in the external magnetic field of the NMR instrument. The circulating electrons generate



a magnetic field that is opposed to the external magnetic field in the center of the ring but is parallel to the external magnetic field outside the ring in the region where the hydrogens are located.

Because the induced field is parallel to the external field where the hydrogens are located, less external field is needed to reach the total field required for the absorption of the electromagnetic radiation and the hydrogens appear at a downfield position. Of course, if a hydrogen is held near the center of the ring, an upfield shift is observed. As an example, the bridges in the following compound force the red proton to sit directly above the benzene ring. This hydrogen appears upfield from TMS at the extremely high field position of −4.03 δ!





This ring current in benzene is termed **diamagnetic** and is characteristic of aromatic compounds in general. The presence of a diamagnetic ring current provides a useful experimental criterion for the presence of aromaticity in a compound. Other examples of the use of this method are provided in Section 16.10.

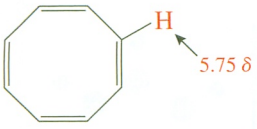
Antiaromatic compounds exhibit a different ring current, termed **paramagnetic,** that induces a magnetic field that is parallel to the external magnetic field in the center of the ring and opposed to it outside the ring. This causes hydrogens on the outside of the ring to appear upfield from the position of normal alkene hydrogen, a result that is exactly the opposite of the effect found with aromatic compounds.

An example of this effect is provided by tri-*tert*-butylcyclobutadiene. This compound is stable at room temperature for a brief time because the bulky *tert*-butyl groups retard the dimerization reaction that destroys less hindered cyclobutadienes. The ring hydrogen of this compound appears at 5.38 δ, a position somewhat upfield from that of the hydrogens of a nonaromatic model compound such as cyclobutene (5.95 δ).

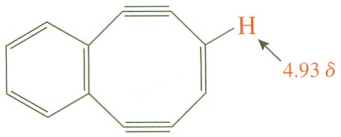
Tri-*tert*-butylcyclobutadiene

Because of its nonplanar geometry, cyclooctatetraene is not antiaromatic and its hydrogens appear at 5.75 δ, a value typical for alkenes. However, the triple bonds of the compound called benzo-1,5-cyclooctadiene-3,7-diyne force this molecule to assume a nearly planar geometry. The pi system of its eight-membered ring contains eight electrons. (Only two of the electrons of each triple bond are part of the conjugated system.)

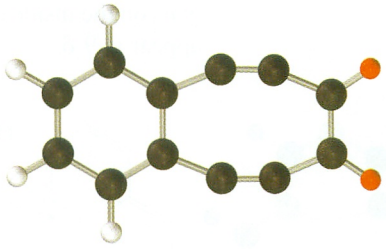
The hydrogens on the double bond of the eight-membered ring appear upfield at 4.93 δ, indicating that this compound has some antiaromatic character.



Cycloactatetraene



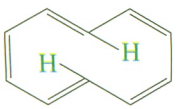
Benzo-1,5-cyclooctadiene-3,7-diyne



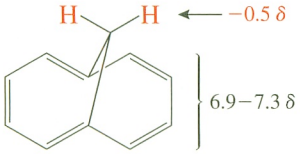
16.10 ANNULENES

The general name **annulene** is sometimes given to rings that contain alternating single and double bonds in a single Lewis structure. Thus, benzene can be called [6]annulene, and cyclooctatetraene can be called [8]annulene. A number of larger annulenes have been prepared to determine whether they follow Hückel's rule and are aromatic when they have $4n + 2$ electrons in the cycle.

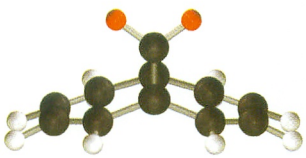
The larger members of this series would have considerable angle strain if they were planar and had only cis double bonds. The incorporation of trans double bonds provides a way to relieve this angle strain, although this often introduces steric strain resulting from atoms on opposite sides of the ring being forced into the same region of space. Consider, for example, [10]annulene. With two trans double bonds it has no angle strain, but the two hydrogens that point into the interior of the ring cause so much steric strain that attempts to prepare this compound have not yet been successful. However, the compound with a CH_2 bridge in place of the offending hydrogens has been prepared. Although the bridge causes the ring to be somewhat distorted from planarity, the compound does show the presence of a diamagnetic ring current typical of an aromatic compound. The hydrogens on the periphery of the ring appear at 6.9 to 7.3 δ, and the hydrogens on the bridge, which are held over the face of the ring, appear at the substantially upfield position of −0.5 δ. (The hydrogens of a typical CH_2 group attached to a carbon–carbon double bond appear near 2 δ.)



[10]Annulene (not yet prepared)

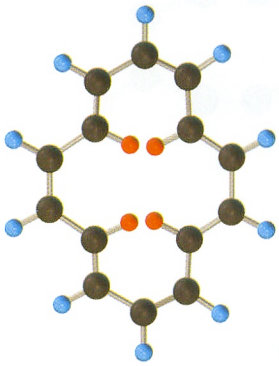


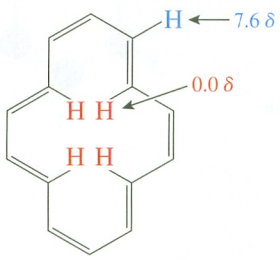
A bridged [10]annulene



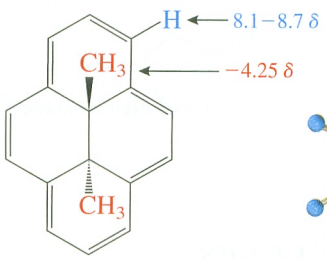
The hydrogens inside the ring of the [14]annulene with four trans double bonds appear at 0.0 δ and the hydrogens on the outside of the ring appear at 7.6 δ, indicating the presence of a diamagnetic ring current. However, the steric strain caused by the hydrogens inside the ring makes this compound quite reactive. The bridged [14]annulene, where these steric interactions are absent, is stable and has many characteristics of an

aromatic compound. The bond distances are all near 1.4 Å, it undergoes substitution reactions rather than addition reactions, the outer hydrogens appear at 8.1 to 8.7 δ, and the hydrogens of the methyl groups appear at -4.25 δ. As a final example, the hydrogens on the inside of the ring of [18]annulene appear at -3 δ and the outside hydrogens appear at 9 δ.

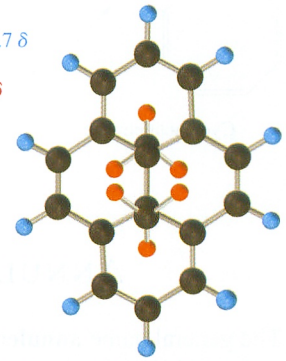


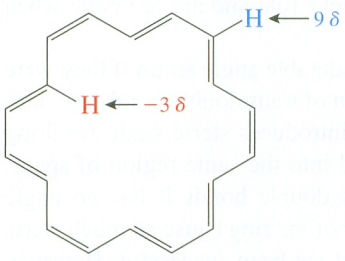


[14]Annulene

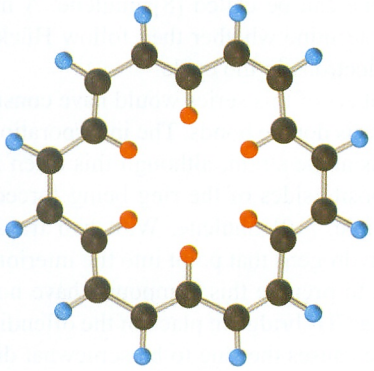


A bridged [14]annulene



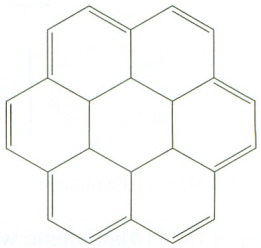


[18]Annulene



PROBLEM 16.11

The ^{1}H-NMR spectrum of this compound shows absorptions in the region of 9.5 δ and other absorptions in the region of -7 δ. Explain which hydrogens are responsible for each of these absorptions.



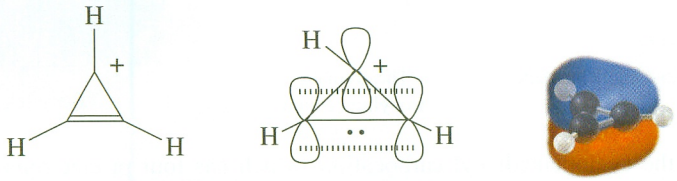
MODEL BUILDING PROBLEM 16.1

Build models of [10]annulene and the bridged [10]annulene discussed on the previous page and examine the strain and planarity of each.

16.11 Aromatic and Antiaromatic Ions

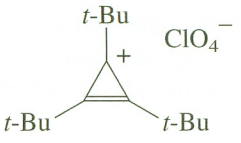
Rings containing an odd number of carbon atoms can be aromatic or antiaromatic, if they are planar and have a conjugated *p* orbital on each ring atom. To have an even number of electrons in their odd number of *p* orbitals, these species must be ionic. They must be carbocations or carbanions.

The simplest example of such an ion is the cyclopropenyl carbocation:



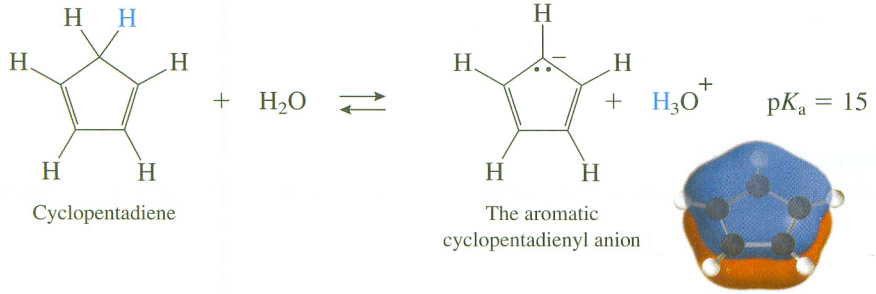
The cyclopropenyl carbocation

Because a carbocation is sp^2 hybridized, with trigonal planar geometry and an empty *p* orbital, this ion has a cycle of three *p* orbitals. (Remember that it is not the number of orbitals that determines whether a compound is aromatic or not, but rather the number of electrons in the pi MOs.) The cyclopropenyl carbocation has two electrons in its three pi MOs, so it fits Hückel's rule and should be aromatic. In fact, cyclopropenyl carbocations are significantly more stable than other carbocations, even though they have considerable angle strain. For example, most carbocations react rapidly with water, a weak nucleophile. In contrast, tri-*tert*-butylcyclopropenyl perchlorate, a carbocation salt, is stable enough to be recrystallized from water.



Tri-*tert*-butylcyclopropenyl perchlorate

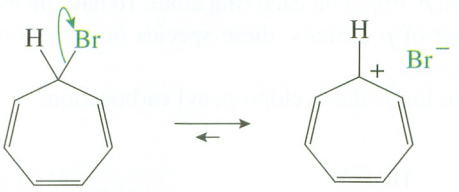
Another example is provided by the acidity of cyclopentadiene. This compound is approximately as strong an acid as water and is many orders of magnitude more acidic than other hydrocarbons because its conjugate base, with six pi electrons, is aromatic.



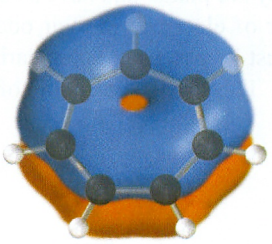
Cyclopentadiene

The aromatic cyclopentadienyl anion

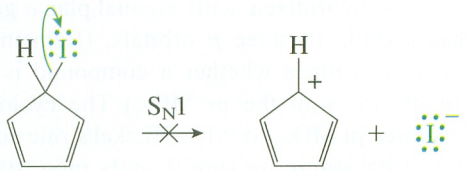
The cycloheptatrienyl carbocation, also known as the tropylium cation, has six pi electrons. It is also aromatic and is quite stable. In fact, 7-bromo-1,3,5-cycloheptatriene actually exists as an ionic compound.



7-Bromo-1,3,5-cycloheptatriene — The aromatic tropylium cation



In contrast, the cyclopentadienyl carbocation, which has four pi electrons and is antiaromatic, is quite unstable. Thus, 5-iodo-1,3-cyclopentadiene is unreactive under conditions in which iodocyclopentane reacts rapidly by an S_N1 mechanism.



5-Iodo-1,3-cyclopentadiene — The antiaromatic cyclopentadienyl cation

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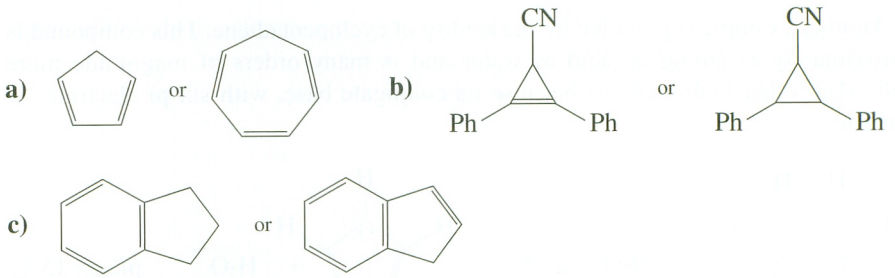
The concept of aromaticity is very important in understanding the chemical behavior of cyclic, conjugated compounds. It is most important with benzene and its derivatives, but it also has applications to many other types of compounds. Whenever a reactant, product, or intermediate contains a planar cycle of *p* orbitals, the effect of aromaticity (or antiaromaticity) on the reaction must be considered.

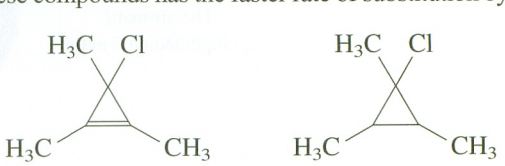
PROBLEM 16.12

Explain which of these compounds is a stronger acid:



PROBLEM 16.13

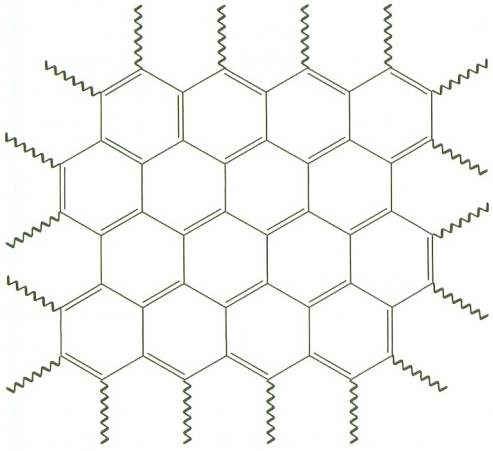
Explain which of these compounds has the faster rate of substitution by the S_N1 mechanism:



Focus On

Buckminsterfullerene, a New Form of Carbon

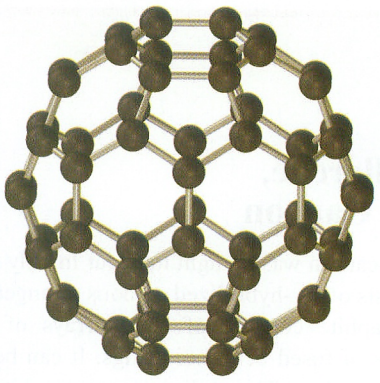
Until recently, elemental carbon was thought to occur in only two forms: diamond and graphite. Diamond consists of sp^3-hybridized carbons arranged in a three-dimensional, tetrahedral network. Graphite consists of large arrays of sp^2-hybridized carbons arranged in planar sheets of fused benzenoid rings. It can be viewed as the ultimate polycyclic aromatic hydrocarbon. The ability of one graphite sheet to slide over another gives it its lubricating properties.



Graphite

Who would have thought that another form of carbon might exist and remain undiscovered until the mid-1980s? In 1985, R. E. Smalley, R. F. Curl, Jr., H. W. Kroto, and their collaborators reported their studies on the products from the vaporization of carbon by a laser. (Smalley, Curl, and Kroto shared the 1996 Nobel Prize in chemistry for this work.) Under certain conditions a relatively large amount of a compound with the formula C_{60} (determined by mass spectrometry) is produced. These scientists proposed that C_{60} is ball shaped and has the geometry of a truncated icosahedron, that is, a polygon with 12 pentagonal faces and 20 hexagonal faces. (The seams of a soccer ball have this geometry.) The structure of this C_{60} molecule is related to that of graphite, with its six-membered benzenoid type rings. However, the presence of the five-membered rings causes the surface of the atoms to curve back on itself so that a spherical shape can be attained. In this manner, all of the carbons can have their valences satisfied without introducing any significant strain into the molecule.

Continued

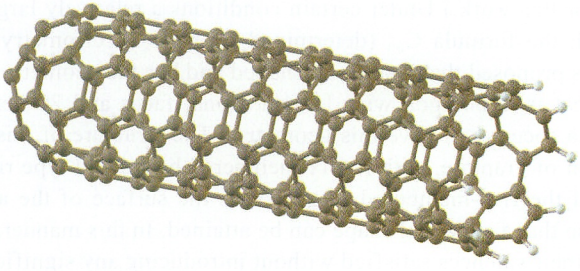


Buckyball

Buckminsterfullerene (or buckyball), named after R. Buckminster Fuller, who was famous for his use of geodesic domes in architecture, was originally produced in minuscule amounts. However, resistive heating of graphite under an inert atmosphere has recently been found to generate significantly larger amounts of this fascinating compound. (In fact, it is now available from a chemical supply company for about $250 for 1 g.) Because of its high symmetry, it has only four absorption bands in its IR spectrum. Its ^{13}C-NMR spectrum is even simpler, consisting of a single peak at 143.2 δ—all 60 carbons are identical!

Research on fullerenes is being reported at a frantic pace. It has been doped with metals to produce materials that are superconducting. Small atoms have been trapped within the hollow cavity of the ball, and chemists are currently attempting to trap other atoms, especially metals, within the cage. The properties of such caged metal atoms may be truly unique.

Larger, nonspherical assemblies of carbon atoms have also been prepared, some with a tubular shape. These so-called nanotubes can be viewed as a rolled-up graphite sheet, perhaps capped with half of a buckyball in some cases. Nanotubes have many potential applications. They may be useful in constructing faster and smaller electronic devices because they can be doped to become semiconducting or metallic and they can be made to carry electrical current at higher densities than metals. They can also be spun into incredibly strong fibers. However, before they can reach their true potential, methods to produce them inexpensively must be developed.



Review of Mastery Goals

After completing this chapter, you should be able to:

- Show the MO energy levels for planar, cyclic, conjugated compounds. (Problem 16.14)
- Apply Hückel's rule and recognize whether a particular compound is aromatic, antiaromatic, or neither. (Problems 16.15, 16.19, 16.20, 16.23, 16.29, and 16.30)
- Understand how aromaticity and antiaromaticity affect the chemistry (and NMR spectra) of compounds. (Problems 16.16, 16.17, 16.18, 16.21, 16.22, 16.24, 16.25, 16.26, 16.28, and 16.31)

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Additional Problems

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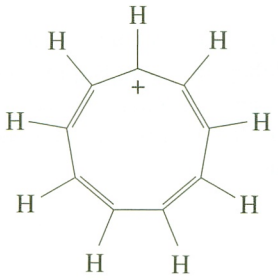
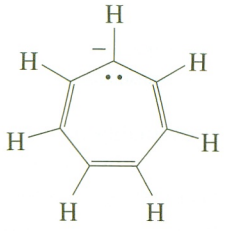
16.14 Show the energy levels for the pi MOs of these species. Show the electrons occupying these MOs.

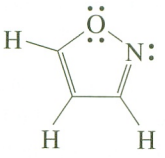
a)

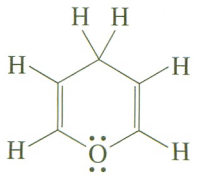
b)

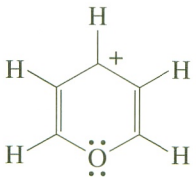
c) 

16.15 Explain whether each of these species is aromatic, antiaromatic, or neither:

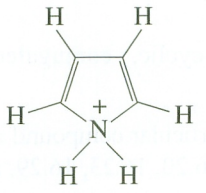
a) 

b) 

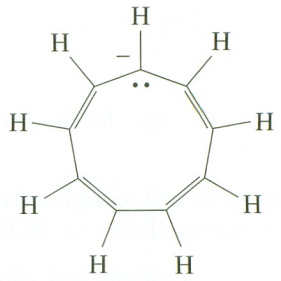
c) 

d) 

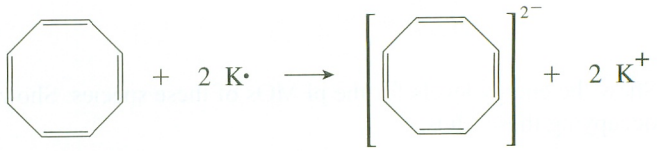
e)



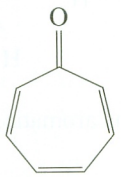
f)



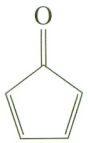
16.16 Cyclooctatetraene readily reacts with potassium metal to form a dianion. Discuss the electronic structure and geometry of this dianion and explain why it is formed so readily.



16.17 2,4-Cyclopentadienone is unstable and cannot be isolated, whereas 2,4,6-cycloheptatrienone is quite stable and is readily isolated. Use arguments based on resonance and aromaticity to explain these experimental observations. (*Hint*: Recall a resonance structure that is commonly written for the carbonyl group.)



2,4,6-Cycloheptatrienone
(stable)



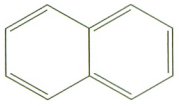
2,4-Cyclopentadienone
(unstable)

16.18 Cyclopropanone is a highly reactive ketone, presumably because of the extra angle strain introduced into the three-membered ring by the sp^2-hybridized carbonyl carbon. Cyclopropenone is much less reactive even though it has more angle strain. Offer an explanation for this experimental observation.

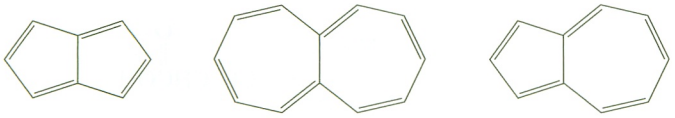
More reactive

Less reactive

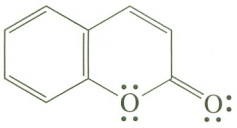
16.19 Hückel's rule applies only to compounds with a single ring, such as benzene and cyclobutadiene. However, it can be used with multiple-ring compounds if the resonance structure with all of the double bonds on the periphery of the ring is considered. For example, using such a structure for naphthalene shows 10 electrons in the cycle, so it is predicted to be aromatic.



Use this to explain why two of the following compounds are very reactive, whereas one is quite stable:

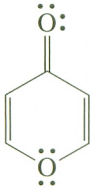


16.20 Coumarin is an important natural flavoring. Explain whether the oxygen-containing ring has any aromatic character.

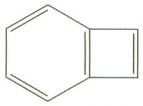


Coumarin

16.21 The conjugate acid of this ketone is quite stable. Explain.

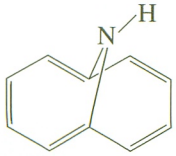


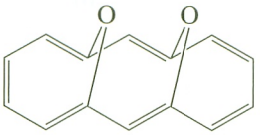
16.22 Benzocyclobutadiene is a very reactive compound. Explain.



Benzocyclobutadiene

16.23 Explain whether these compounds are aromatic or not:

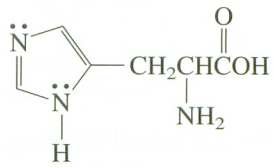
a) 

b) 

16.24 Predict the approximate positions for the absorptions in the ^{1}H-NMR spectrum of this compound.

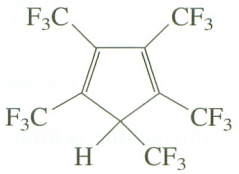
BioLink

16.25 The amino acid histidine contains an imidazole ring. In many enzymes this ring acts as a basic catalyst. Explain which nitrogen of the imidazole ring is more basic and show the structure of the conjugate acid of imidazole.



Histidine

16.26 This compound is a stronger acid than nitric acid. Explain.

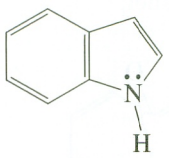


16.27 The heat of hydrogenation of pyrrole is 31.6 kcal/mol (132 kJ/mol). The heat of hydrogenation of cyclopentene is 26.6 kcal/mol (111 kJ/mol). Calculate the resonance stabilization of pyrrole.

16.28 The following compound reacts with butyllithium to form $C_8H_6^{2-}$. Suggest a structure for this dianion and explain its ready formation.

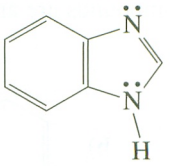
16.29 Fused heterocyclic compounds are similar to polycyclic aromatic compounds except that one or more of the fused rings is a heterocycle. Explain whether or not the heterocyclic rings of these compounds are aromatic.

a)



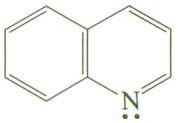
Indole

b)



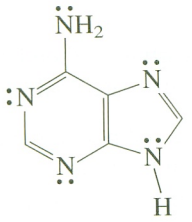
Benzimidazole

c)



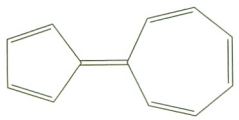
Quinoline

16.30 Adenine is an important base that is found as a component of DNA. Explain whether adenine is aromatic or not.



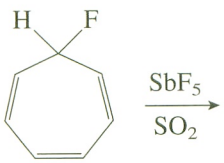
Adenine

16.31 Derivatives of this compound have been found to have large dipole moments. Use resonance and the theory of aromaticity to explain this observation.

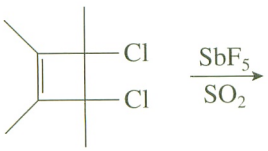


Problems Involving Spectroscopy

16.32 When 7-fluoro-1,3,5-cycloheptatriene is dissolved in SbF_5/SO_2, a species is produced that shows a singlet near 9.2 δ in its ^{1}H-NMR spectrum. Show the structure of this species and explain why the absorption is so far downfield.



16.33 When this dichloride is dissolved in SbF_5/SO_2, a species is produced that shows only two absorptions in its ^{13}C-NMR spectrum. One of these signals appears at 209 δ. Show the structure of this species and explain why the signal is so far downfield.



16.34 The fragmentation in the mass spectrometer of the molecular ion of aromatic compounds to produce benzylic carbocations was discussed in Section 15.6. Actually, the benzylic carbocation is thought to rearrange to an even more stable carbocation, also with *m/z* 91, that is the actual species that is detected. Suggest a structure for this carbocation and explain why it is so stable.

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16.35 Explain which of the carbon–carbon bonds in this model of cyclooctatetraene are single bonds and which are double bonds.

16.36 Purine is a heterocyclic compound with four nitrogen atoms. Each N has a pair of electrons on it in the Lewis structure. Explain which of these pairs are part of the pi system and which are not. Explain whether purine is aromatic or not.

16.37 For each of these heterocyclic compounds, explain which electron pairs are part of the pi system and which are not. Explain whether each compound is aromatic or not.

16.38 Explain why fluorene is a much stronger acid than most hydrocarbons. Its pK_a is 23.

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